DEGRADATION OF DIRECT BLACK 38 DYE CATALYZED BY LAB PREPARED NICKEL HYDROXIDE IN AQUEOUS MEDIUM

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ABSTRACT

This study is focused on degradation of Direct Black dye, a common azo dye, catalyzed by nickel hydroxide in aqueous solution. Nickel sulfatehexahydrate, sodium hydroxide and sodium hypochlorite were used for synthesis of nickel hydroxide catalyst. The catalytic performance of nickel hydroxide for oxidative degradation of Direct Black dye was examined in terms of discrete parameters like effect of temperature, concentration of dye, stirring speed, time of reaction etc. Curve Expert software was used for kinetics analysis of batch experimental data. Degradation reaction was taking place according to Langmuir-Hinshelwood mechanism. According to this mechanism the reactants react in adsorbed form at the surface of nickel hydroxide catalyst.

Key Words: Direct Black 38 dye; Kinetics analysis; Langmiur-Hinshelwood mechanism; Adsorption; Activation energy

1. Introduction

Accelerated industrialization has expanded the demand for synthesis of a wide range of materials and chemicals in everyday life. One of these industries is the textile industry which uses chemicals as dyes in huge amount. It has been estimated that textile industry releases about 20% of these dyes in environment as wastewater (Bhatti *et al.*, 2014; Sathiya *et al.*, 2007; Khan *et al.*, 2014; Ioannis *et al.*, 2004). Water contaminated with dyes imparts colors to the water resources which block the access of solar radiations to the interior of water body resulting in disturbance of aquatic life. Elimination of dye stuffs from industrial effluents has, therefore, received much attention in recent years. Traditional techniques like coagulation by chemical agents, reverse osmosis, adsorption on carbon, ultrafiltration, ion exchange on synthetic adsorbent resins, etc can generally be employed for the removal of dye pollutants (Song *et al.*, 2009).

About half of the dyes employed in textile industry are azo dyes which composed of diazotizedamine connected to phenol or amine. These dyes are characterized by presence of a single or multiple azo (–N=N–) linkages. These dyes are considered as carcinogenic and tumorigenic material (Kamboh *et al.*, 2014; Ghaedi *et al.*, 2012). The structures of these dyes are complex due to presence of aromatics and synthetic

origin. These dyes are eminently permanent, resistant against biological and photo degradation and chemical oxidation. As a result, conventional physio-chemical and biochemical techniques for oxidation/degradation of these azo dyes become ineffective (Arsalan *et al.*, 2001; Vandeviere *et al.*, 1998). Consequently, conventional techniques dealing with effluent containing these refractory azo dyes, e.g. reactive dyes, are unable to meet effluent color standards. Therefore, search of other substitute for the removal of these dyes from environment has received much attention. Wet oxidation, the oxidation of organic pollutants in aqueous system at elevated temperature and pressure, can be considered as feasible and convenient alternative technique. However economic factor does not favor this technique due to high temperature and pressure. The cost of wet oxidation process can be lowered by employing suitable heterogeneous or homogenous catalysts (Saeed and Ilyas, 2013). Various homogeneous catalysts have shown excellent activities for degradation of dyes in aqueous phase; however metal ions leach to aqueous phase which results in another environmental problem. Hence wet oxidation employing heterogeneous catalysts can be considered as best protocol for degradation of dyes in waste water. In this technique various bulk and supported catalysts can be employed for mineralization of dyes in aqueous medium. Various oxidative agents like hydrogen peroxide, oxygen, or air can be used in this technique (Ilyas and Saqiq, 2007, 2008; Ilyas and Saeed, 2009).

This paper is therefore aimed to evaluate the catalytic efficiency and practical feasibility of lab prepared nickel hydroxide towards degradation of the Direct Black 38 azo dye in aqueous medium.
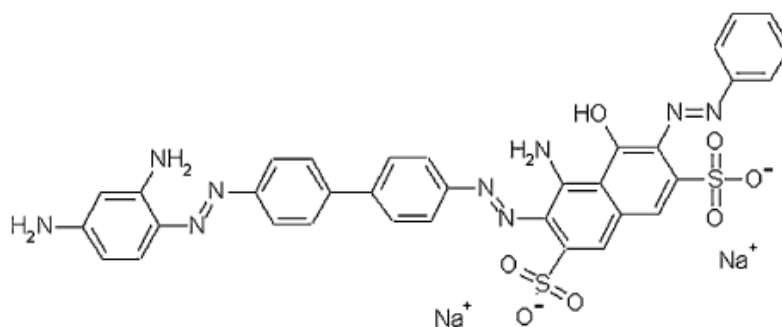
Image 1: Direct Black 38 dye

2.   Materials and methods

2.1. Materials

Analytical grade $NiSO_4·6H_2O$, $NaClO$, $NaOH$, $AgNO_3$, KIO_3, KI, $Na_2S_2O_3·5H_2O$, H_2O_2 and CH_3COOH were used without further purification. Direct Black 38 dye was obtained from local market of Faisalabad Pakistan.

2.2. Preparation of catalyst

Nickel hydroxide catalyst was prepared by precipitation method. A solution was prepared by taking nickel sulfatehexahydrate (130g) in distilled water (300 ml). Another solution was prepared by taking sodium hydroxide (42g) in 6% sodium hypochlorite solution (300 ml). Solution of sodium hydroxide was added drop wise to nickel sulfatehexahydrate solution while stirring continuously at 293 K. Black nickel hydroxide was precipitated. The precipitated black nickel hydroxide was filtered from the reaction mixture. The precipitate was washed with double distilled water till negative test of chlorine in drain was detected by silver nitrate. After drying at 383 K for 24 hours, it was sized, sieved and stored in stoppered bottle.

2.3. Characterization of the catalyst

The prepared nickel hydroxide was characterized by FTIR, XRD, SEM and surface area and pore size analysis as described earlier (Saeed and Ilyas, 2013).

For measurement of total oxygen content of the nickel hydroxide, about 2 g of potassium iodide was dissolved in 20 ml of 36% acetic acid solution. About 0.2 g nickel hydroxide was added to this solution and was left for 15 minutes under inert atmosphere to release iodine. After filtration, the released iodine was titrated with sodium thiosulfate solution (0.1 N). Similarly about 0.2 g nickel hydroxide and 2 g potassium iodide were mixed in buffer of pH 7.1 (15 ml) and mixture was stirred for 15 minutes in inert atmosphere for exploration of surface oxygen content of nickel hydroxide. After filtration, 2 ml of 1N HCl was added. Iodine was titrated with sodium thiosulfate solution. Following equation was used to determine the oxygen content.

$$Oxygen_{(gatmOxygen/gCatalyst)} = \frac{Na_2S_2O_3(mL) \times N(Na_2S_2O_3)}{1000 \times Catalyst(g) \times 2} \tag{1}$$

3.5×10^{-4} and 2.9×10^{-4} g-atom oxygen g^{-1} were determined as total oxygen content and surface oxygen content of nickel hydroxide respectively.

2.4 Degradation protocol

Degradation experiments of Direct Black dye with nickel hydroxide catalyst were carried out at 313, 323, 333 K using 300, 400 and 500 ppm as initial concentration of dye. For a typical run, 40 ml dye solution was stirred continuously in batch reactor at specified temperature. After stirring the solution for 30 minutes at desired temperature, 0.5 ml sample was withdrawn from reactor to observe any variation in concentration during the heating and stirring period. Hydrogen peroxide (1 ml) was added as oxidant to reactor while stirring the reaction mixture continuously. After 30 minutes stirring, again 0.5 ml sample was withdrawn from reactor to observe any variation in concentration of dye solution. Then 0.05 g catalyst was added to reaction mixture and stirred continuously. At appropriate time intervals, 0.5 ml samples were taken from reactor. UV-Visible spectrophotometer was used for analyses of reaction mixture. The absorbance of the samples was measured by spectrophotometer at 530 nm which corresponds to the maximum absorbance of Direct Black 38 dye. The absorbance was converted to concentration using standard curve of black dye. HPLC (Agilent Technologies) was used to determine inorganic products and the reaction intermediates. The percent degradation of Direct Black dye was computed using following equation.

$$Conversion\ (\%) = \frac{[DB]_o - [DB]_t}{[DB]_o} \times 100 \tag{2}$$

Where $[DB]_o$ and $[DB]_t$ represent the concentration of dye at the beginning of reaction and different time interval respectively.

3.   Results and discussions

3.1. Oxidative degradation

Fig. 1 shows the profile data of nickel hydroxide catalyzed oxidative degradation of Direct Black dye in aqueous medium. This investigation was accomplished with 40 ml (300 ppm) solution of Direct Black dye in the presence of 1 ml hydrogen peroxide and 0.05 g nickel hydroxide catalyst while stirring the reaction mixture at 500 rpm. Separate experiments were performed at 313, 323 and 333 K. About 18% degradation of 300 ppm Direct Black 38 dye solution was noted in first 15 minutes and was gradually increased to 59% after 120 minutes at 313 K. Similarly 22% degradation was achieved in 15 minutes at 323 K which was increased to 71% after 120 minutes. Finally, at 333 K, the degradation was 28% within 15 minutes and increased to 88% after 2 hours as given in Fig. 1. This figure indicates that temperature greatly affect the degradation of dye. Collazzo *et al.* 2012 have reported 60% degradation of 55 ppm solution of Direct Black 38 dye in 6 hours at 298 K using N-doped TiO_2 as photo catalyst under UV and sunlight irradiation. Similarly 80% mineralization of different dyes including black dye with oxygenated-UV-ZnO system has been reported by Gouvêa and his co-workers (Gouvêa *et al.*, 2000) in 120 minutes of reaction time. Saggioro

and co-workers (Saggioro *et al.*, 2011) have studied complete decolorization of 30 ppm solution of black dye using 1 gL^{-1} of TiO$_2$ as photo catalyst under UV irradiation.
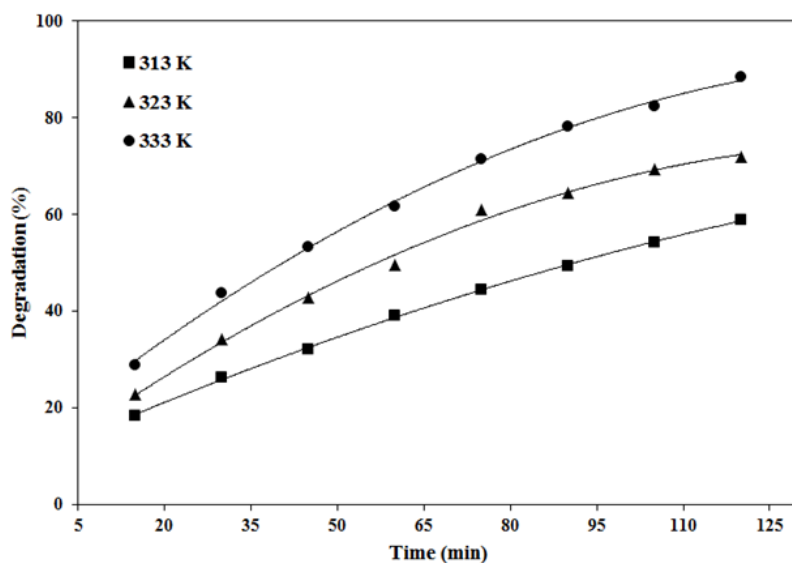
Figure 1. Time profile of oxidation/degradation of Direct Black dye over nickel hydroxide catalyst at various temperatures. Reaction Conditions: Black dye 300 ppm, Catalyst 0.05 g, Stirring speed 500 rpm, Hydrogen peroxide 1 ml

To estimate the degree of the thermal degradation of Direct Black dye, experiments were carried out with 300 ppm as the initial dye concentration, in the absence of nickel hydroxide catalyst for 60 minutes. It was noted that there was no appreciable change in concentration of dye which confirm that nickel hydroxide in present investigation acts as an active catalyst for oxidative degradation of Direct Black dye in aqueous medium. The cleavage often takes place on the azo linkage (−N=N−) of the aromatic azo compounds, because these π bonds are comparatively more diffusive than other parts within the molecule. Ultimately black dye was completely degraded to water and carbon dioxide; however existence of benzene sulfonate, naphthoquinone and carboxylic acids like pthalic, fumaric, succinic, maleic, malonic, oxalic and formic acids was noted with HPLC. These compounds were finally mineralized to water and carbon dioxide (Chu *et al.*, 2008; Sauer *et al.*, 2006).
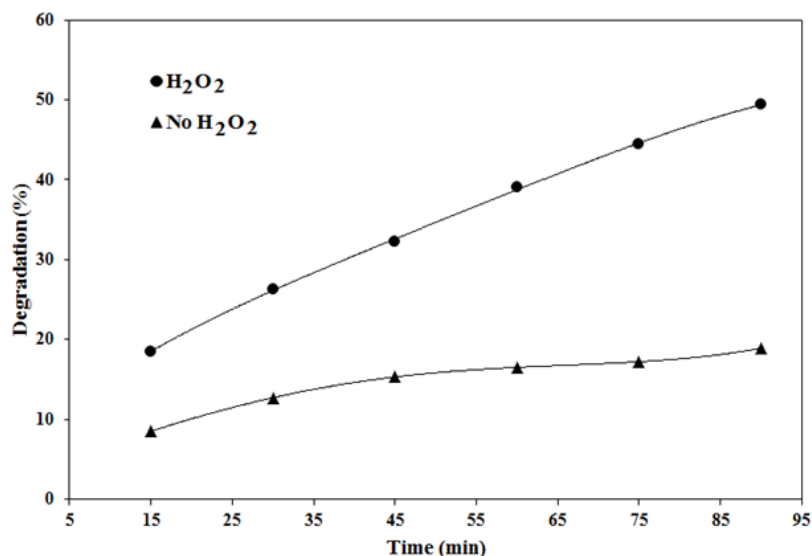
3.2. Role of hydrogen peroxide on degradation of dye

The effect of hydrogen peroxide on degradation of Direct Black dye was examined by carrying out separate experiments in presence and absence of hydrogen peroxide at 313 K. This investigation was accomplished by taking 40 ml of dye solution (300 ppm) and 0.05g of catalyst in batch reactor. Fig. 2 depicts the comparison of degradation of Direct Black dye with and without hydrogen peroxide. Figure shows that about 19% degradation of dye achieved in 90 minutes in absence of hydrogen peroxide which was increased to 50% with hydrogen peroxide. In the reaction where no hydrogen peroxide was added, the dissolved oxygen in water takes part in degradation of dye. This study declares that hydrogen peroxide acts as oxidant in catalytic degradation of dye in aqueous medium.

3.3. Catalyst leaching

Catalyst leaching is a hindrance in heterogeneous reactions, where liquid phase reactants are involved. To confirm catalyst leaching in present study, following procedure was adopted. First water, the solvent (40 ml), and nickel hydroxide catalyst (0.05g) were taken in reactor. The reaction mixture was continuously stirred at 323 K for 1 hour. The catalyst was separated from reaction mixture in second step and 0.02 mmol black dye was added to get 300 ppm dye solution. The reaction mixture was stirred at 500 rpm in the presence of hydrogen peroxide for one hour. Analysis of reaction mixture showed that there

was no appreciable decrease in concentration of dye, confirming the absence of leaching of the nickel hydroxide. The absence of leaching was further assured by dimethyl glyxime test. The absence of coloration with dimethyl glyxime test assured the absence of nickel ions and hence nickel hydroxide in present investigation is heterogeneous in nature (Charlot, 1964; Ilyas and Saeed, 2009; Saeed and Ilyas, 2013).

Figure 2. Comparison of degradation of Direct Black dye in presence and absence of hydrogen peroxide. Reaction conditions: Direct Black dye 300 ppm, Temperature 313 K, Catalyst 0.05g, Agitation 500 rpm

3.4. Effect of initial concentration

Fig. 3 shows the % degradation of Direct Black dye vs time with 300, 400 and 500 ppm as initial dye concentrations at 313 K over 0.05 g of catalyst while stirring the reaction mixture at 500 rpm.
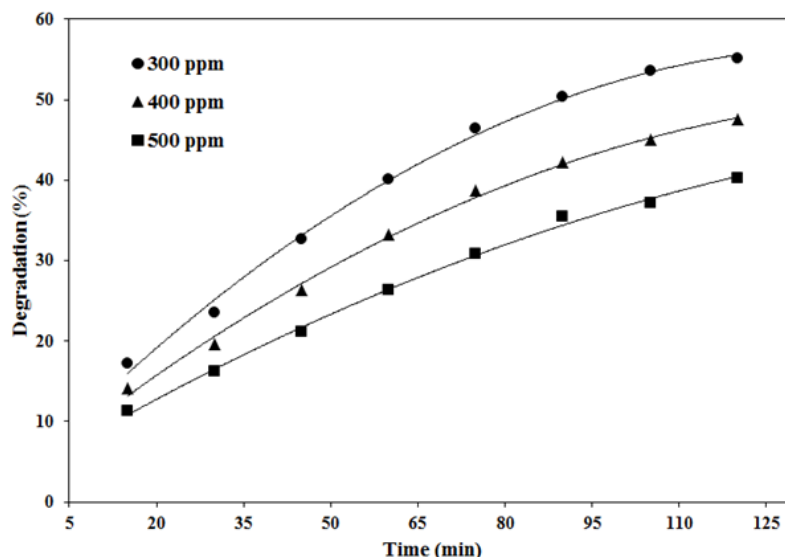

Figure 3. Time profile of oxidation/degradation of Direct Black 38 dye over nickel hydroxide catalyst at various initial concentration of Direct Black dye. Reaction Conditions: Temperature 313 K, Catalyst 0.05 g, Stirring speed 500 rpm, Hydrogen peroxide 1 ml

As the initial concentration of dye increases, the degradation decreases. It is assumed that as the initial dye concentration increases, the imposed catalyst loading along with the fixed agitation speed does not allow a complete conversion of black dye. This is due to transport limitations of dye to the catalyst surface. The effect of decrease in conversion of dye with increase in initial concentration of dye can be indicative of some kind of dye self-inhibition. For this reason the effect of the catalyst loading and speed of agitation has been investigated (Resini *et al.*, 2008).

3.5. Effect of catalyst dose

The influence of catalyst dose on degradation of black dye was investigated with catalyst dosage of 0.025-0.125g with 300 ppm (40 ml) of dye solution in the presence of hydrogen peroxide at 313K. The degradation of black dye increases with dose of catalyst in the range of 0.025-0.05 g and then decreases with dose of catalyst in the range of 0.075-0.125g. Similarly degradation of dye per unit time and per unit mass of the catalyst also increases initially with catalyst dose from 0.025 to 0.05 g and then decreases in range of 0.075 to 0.125g of catalyst dose. These results are shown in Fig. 4.
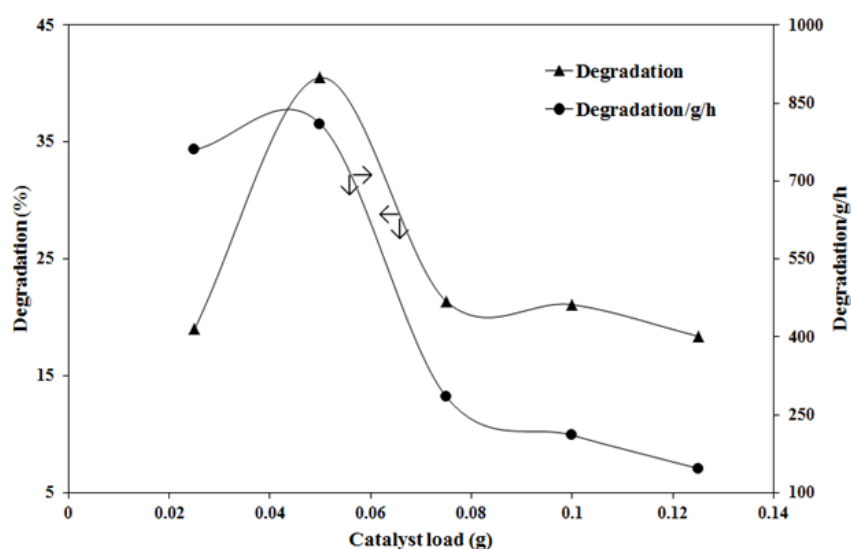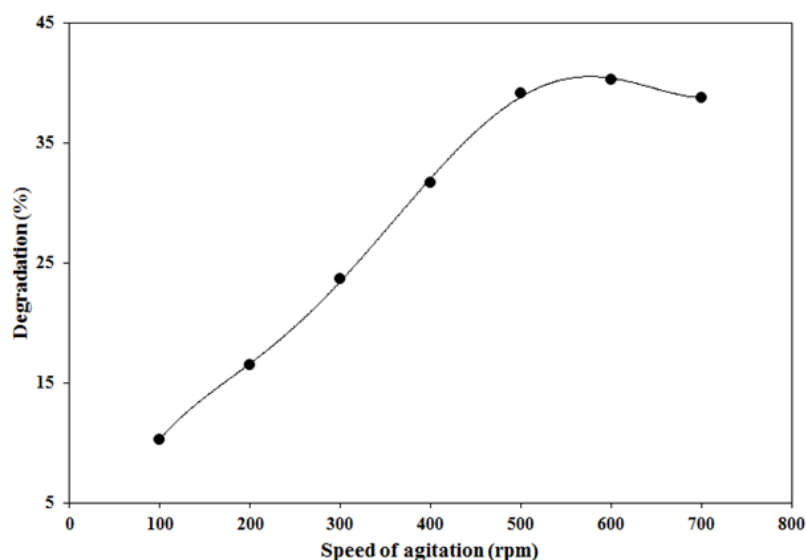

Figure 4/ Effect of catalyst dose on oxidation/degradation of Direct Black dye over nickel hydroxide. Reaction Conditions: Direct Black dye 300 ppm, Temperature 313 K, Time 60 minutes, Hydrogen peroxide 1 ml, Stirring speed 500 rpm

At higher catalyst dose, the reaction mixture can't be agitated homogeneously at given stirring speed, resulting in decrease in degradation of dye with catalyst loading. Increasing the stirring speed, the reaction mixture can be agitated homogeneously; however increase in stirring speed result in splashing of the reaction mixture. Catalyst dose of 0.05g was selected as optimum amount of catalyst and was used in all experiments.

3.6. Effect of stirring speed

Nickel hydroxide catalyzed oxidative degradation of Direct Black dye in present study is a slurry-phase reaction having liquid reactants and solid catalyst. In a batch reactor, the mixture was stirred vigorously in order to slurry the catalyst uniformly throughout the liquid. In order to observe the consequences of the speed of agitation on the degradation rate of dye, experiments were performed at different stirring speeds in the range of 100 to 700 rpm (Fig. 5). As the stirring speed increases from 100 to 500 rpm, the rate of degradation increases indicating the mass transfer regime. From 500 to 700 rpm, no appreciable differences on degradation were detected. Stirring speed of 500 rpm is the threshold value at which the resistance due to dye mass transfer to the catalyst particle has overcome. Stirring speed of 500 rpm was selected as optimum stirring speed (Saeed *et al.*, 2013).

Figure 5. Effect of stirring speed on oxidation/degradation of Direct Black over nickel hydroxide. Reaction Conditions: Direct Black dye 300 ppm, Catalyst 0.05 g, Temperature 313 K, Time 60 minutes, Hydrogen peroxide 1 ml

3.7. Re-use of catalyst

To find out the reusability of catalyst, used catalyst was dried at 383 K after washing with ethanol and water several times. It was re-used as catalyst for degradation of dye under identical conditions. It was observed that used catalyst exhibited the same catalytic performance for degradation of dye as the fresh sample as given in Fig. 6.
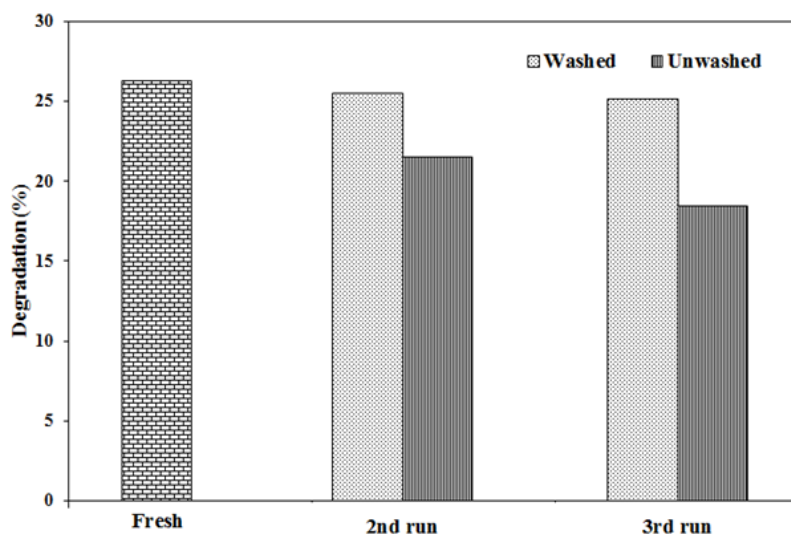
Figure 6. Re-use of nickel hydroxide catalyst in degradation of Direct Black dye. Reaction Conditions: Direct Black dye 300 ppm, Temperature 313 K, Catalyst 0.05g, Agitation 500 rpm, Hydrogen peroxide 1 ml

Similarly the used catalyst was also tested for re-usability without washing of catalyst. Un-washed used catalyst also exhibited almost the same catalytic activities. It can be concluded that the present process is an efficient and convenient protocol for degradation of Direct Black dye in presence of easily separable and reusable nickel hydroxide catalyst.

3.8. Reaction kinetics

Although the rates of surface catalyzed reactions are complex; however the rates can be simplified by quasi-equilibrium and quasi-steady state hypotheses (Salmi *et al.*, 2002). The kinetics of nickel hydroxide catalyzed degradation in present study can be described by power rate law.

$$Rate=k_r[DB]^m[H_2O_2]^n \tag{3}$$

As hydrogen peroxide is in excess in present case; therefore the rate expression becomes as

$$Rate=k[DB]^m \tag{4}$$

Where k and m represents apparent rate constant and order of reaction with respect to dye respectively.

On integration, equation 4 changes to

$$\ln\frac{[DB]_o}{[DB]_t}=kt \tag{5}$$

Where $[DB]_o$ and $[DB]_t$ represent the concentration of Direct Black dye in the beginning of reaction and after different time interval respectively.

Table 1. Kinetics parameters determined by fitting 1st order rate expression to time profile data of degradation of direct black dye

T (K)	k (min^{-1})	R^2
313	0.0077	0.95
323	0.0114	0.96
333	0.0171	0.98

Equation 5 was fitted to experimental data from Fig. 1 as given in Fig. 7. The straight lines show 1st order dependence of rate on the concentration of dye. Table 1 lists the apparent rate constants, k, which were determined from the slops of the straight lines in Fig. 7. However, this approach has limited services, therefore the way of fitting the batch experimental data to Langmuir-Hinshelwood (L-H) mechanism was followed (Ilyas and Sadiq, 2007; Saeed and Ilyas, 2013; Wu *et al.*, 2005; Saeed *et al.*, 2012). According to this mechanism the surface catalyzed reaction takes place in two steps. In first step the reactants adsorb on the surface of the catalyst. In second step the adsorb reactants react and give the final products. According to Langmuir-Hinshelwood (L-H) mechanism, the rate expression for present study can be written as

$$Rate=k_r\theta_{DB}\theta_{H_2O_2} \tag{6}$$

Where k_r, θ_{DB} and $\theta_{H_2O_2}$ represents rate constant, surface covered by Direct Black dye and hydrogen peroxide respectively.

Adsorption of dye and hydrogen peroxide on the surface of catalyst may take place either according to Langmuir, Temkin or Freundlich adsorption isotherm. Langmuir adsorption isotherm may be either competitive or non-competitive. For competitive Langmuir adsorption of dye and hydrogen peroxide, the rate of reaction can be expressed as

$$Rate=k_r\frac{K_{DB}[DB]K_{H_2O_2}[H_2O_2]}{\left(1+K_{DB}[DB]+K_{H_2O_2}[H_2O_2]+K_P[P]^2\right)} \tag{7}$$

K_{DB}, $K_{H_2O_2}$ and K_P represent adsorption coefficient for Direct Black dye, hydrogen peroxide and products respectively.
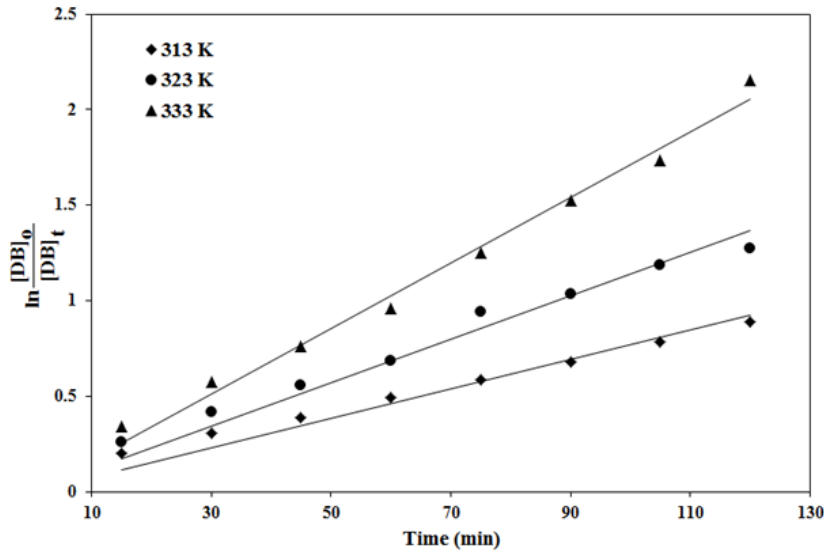
Figure 7. Fitting of 1st order kinetic expression to time profile data of degradation of Direct Black dye

Adsorption-desorption processes are fast enough to be assumed at equilibrium. Hence the expression can be simplified as

$$Rate = k_r \frac{K_{DB}[DB]K_{H_2O_2}[H_2O_2]}{\left(1+K_{DB}[DB]+K_{H_2O_2}[H_2O_2]\right)^2} \tag{8}$$

As hydrogen peroxide is constant in present investigation, therefore equation 8 transforms to

$$Rate = \frac{ab[DB]}{(c+b[DB])^2} \tag{9}$$

Where a, b and c are $k_r K_{H_2O_2}[H_2O_2]$, K_{DB} and $1+K_{H_2O_2}[H_2O_2]$ respectively.

For non-competitive adsorption of Direct Black dye and hydrogen peroxide at the surface of catalyst, the rate expression is

$$Rate = k_r \frac{K_{DB}[DB]K_{H_2O_2}[H_2O_2]}{\left(1+K_{DB}[DB]\right)\left(1+K_{H_2O_2}[H_2O_2]\right)} \tag{10}$$

For constant concentration of hydrogen peroxide, the rate expressions is given by equation 11.

$$Rate = \frac{ab[DB]}{1+b[DB]} \tag{11}$$

Considering Temkin adsorption isotherm, the rate expression is given by

$$Rate = k_r(K_1 \ln K_2[DB])(K_1 \ln K_2[H_2O_2]) \tag{12}$$

Where K_1 and K_2 are two constants. For constant concentration of hydrogen peroxide, the rate equation can be modified as equation 13.

$$Rate = \bar{k}_r(K_1 \ln K_2[DB]) \tag{13}$$

Plot of ln[DB] against rate gives straight line.

Similarly in case of Freundlich adsorption isotherm, rate can be expressed as

$$\text{Rate} = k_r K_{DB}[DB]^{1/n} K_{H_2O_2}[H_2O_2]^{1/n} \tag{14}$$

For constant concentration of hydrogen peroxide

$$\text{Rate} = \overline{k_r} K_{DB}[DB]^{1/n} \tag{15}$$

Plot of ln[DB] against ln rate gives straight line. It is not necessary that both the reactants will adsorb on the surface according to same adsorption isotherm. Direct Black dye and hydrogen peroxide may follow different adsorption isotherms. Under this condition the rate expression may have various forms.

The experimental data at different temperatures from Fig. 1 was analyzed according to these kinetics models. Non-linear least square method of analysis was performed with Curve Expert. Third order polynomial was applied for determination of rates of reaction at different time intervals. Non-competitive Langmuir model (equation 11) was found applicable to the data indicating that the adsorption of Direct Black dye at the surface of catalyst takes place at homogenous surface with infinite number of identical cites. Fig. 8 depicts the fitting of experimental data non-competitive Langmuir model (equation 11). Values of rate constants and adsorption equilibrium constants were determined and are listed in Table 2. Rate constants determined by Langmuir model are true rate constants because the contributions of adsorption equilibrium constant of Direct Black dye have been excluded from these values.
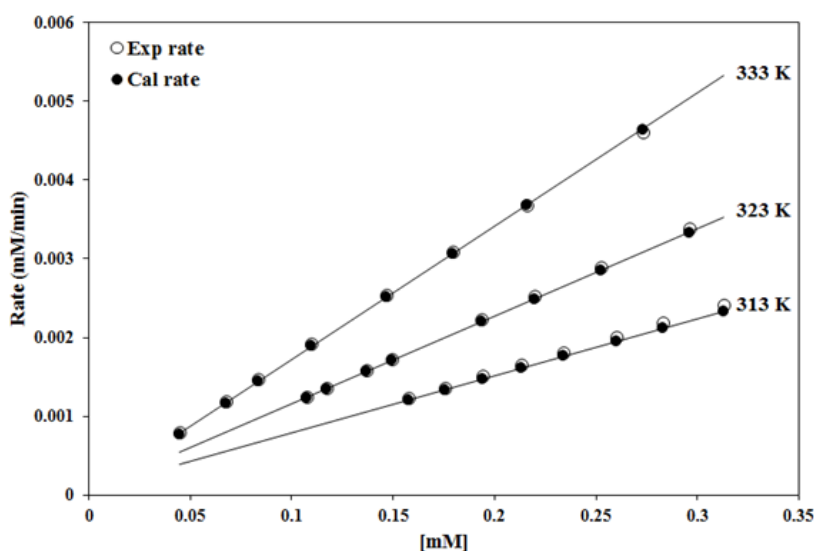
Figure 8. Fitting of Langmuir model (equation 11) to time profile data of nickel hydroxide catalyzed degradation of Direct Black dye using Curve Expert software

3.9. Energy of activation

Arrhenius equation was applied to rate constants at various temperatures from Table 1 and 2 for determination of activation energy. As Table 1 lists apparent rate constants, so energy of activation determined by these rate constants is apparent activation energy, E_{Ap}. Similarly Table 2 lists true rate constants; hence the activation energy determined is true activation energy, E_T. 34.6 and 62.7 kJ mol^{-1} were determined as apparent and true activation energy respectively. vant's Hoff isochore (equation 16) was used for determination of Enthalpy (ΔH_a), entropy (ΔS_a) and Gibb's energy (ΔG_a) and were found as $-$ 28.1 kJ mol^{-1}, -105.1 J mol^{-1} and -4.8 k Jmol^{-1} respectively.

$$\frac{d\ln K_{DB}}{dT} = \frac{\Delta H_a}{RT^2} \tag{16}$$

Table 2. Kinetics parameter determined by application of Langmuir model (equation 11) to time profile data of nickel hydroxide catalyzed degradation of direct black dye using Curve Expert software

T (K)	k (min^{-1})	K_{DB} (l mol^{-1})	R^2
313	0.051	0.153	0.999
323	0.093	0.125	0.999
333	0.218	0.079	0.999

4. Conclusions

This study reveals that nickel hydroxide which is much cheaper in comparison to commonly used catalysts like Pt and Pd can be employed as an effective catalyst for oxidative degradation of Direct Black dye in aqueous medium. The catalyst was heterogeneous in nature and the oxidative degradation reaction was taking place in kinetic control regime, free from diffusion control regime. Catalytic oxidative degradation of Direct Black dye in present investigation follows Langmuir-Hinshelwood (L-H) type mechanism. According to this mechanism, the reactants react in adsorbed form at the surface of catalyst. Adsorption of Direct Black dye at the surface of catalyst followed non-competitive Langmuir adsorption isotherm. – 28.1, 34.6 and 62.7 kJ mol^{-1} were determined as heat of adsorption, apparent activation energy and true activation energy respectively.

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